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Effect of a Series Connection of a Bi-Electrolyte Hydrogen Sensor in a Leak Detector

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Abstract

Conventional leak detectors are widely based on helium gas sensors. However, the usage of hydrogen sensors in leak detectors has increased because of the high prices of helium leak detectors and the dearth in the supply of helium gas. In this study, a hydrogen leak detector was developed using solid-state hydrogen sensors. The hydrogen sensors are based on Park–Rapp probes with heterojunctions made by oxygen-ion conducting Yttria-stabilized zirconia and proton-conducting In-doped $CaZrO_3$. The hydrogen sensors were used for determining the potential difference between air and air balanced 5 ppm of H_2. Even though the Park–Rapp probe shows an excellent selectivity for hydrogen, the sensitivity of the sensor was low because of the low concentration of hydrogen, and the oxygen on the surface of the sensor. In order to increase the sensitivity of the sensor, the sensors were connected in series by Pt wires to increase the potential difference. The sensors were tested at temperatures ranging from 500–600°C.

Keywords: Hydrogen sensors, YSZ, CZI, Bi-electrolyte, Leak detectors

1. INTRODUCTION

Vacuum annealing is essential in OLED designing and semiconductor manufacturing processes. However, during these processes, toxic gases are often used, and therefore, a leak in the annealing machine can be extremely dangerous. Further, a leak at the connecting section of the machine may lead to an explosion. Therefore, proper leak detectors are required to ensure accuracy, precision, and safety of the process [1].

Conventional leak detectors use helium gas sensors for leak detection. However, although helium is stable and inert, it is expensive, and therefore, it is not economical to use for detection. Consequently, leak detectors using hydrogen gas sensors were developed to overcome such drawbacks [2].

Hydrogen gas sensors can be classified into three types: resistive, electrochemical, and electrolyte. The resistive type sensor uses the properties of an oxide such as tin oxide, and the resistance is dependent on the concentration of H_2. However, the resistance also changes when the sensor is exposed to substances such as CO and ethanol. Therefore, it is difficult to use resistive type sensors as leak detectors [3].

The electrochemical type sensor uses liquids for the measurement of potential differences. It can determine the amount of hydrogen by reactions. However, in low temperatures, the reaction rate is low, and therefore, it becomes difficult to measure the concentration of H_2 leaking from the equipment at room temperature [4].

The electrolyte type sensor measures the concentration of hydrogen ions using the potential difference created by the difference between the standard hydrogen ion concentration and the hydrogen ion concentration that we need to measure. However, it has a drawback in that it is difficult to retain the standard concentration of the hydrogen ions [5].

Conventionally, hydrogen sensors are based on the potential difference created by the difference of H_2 concentrations of outer space and the standard concentration. In this research, a Park–Rapp probe was used as a hydrogen sensor, which comprises a proton conductor ($CaZr_{0.9}In_{0.1}O_{3-\delta}$) and an oxygen ion conductor (yttria-stabilized zirconia). Yttria-stabilized zirconia (YSZ) was used as the standard hydrogen ion concentration detector, by the equilibrium of the reactions between oxygen ions and hydrogen ions [6].

Although the Park–Rapp probe indicated an excellent

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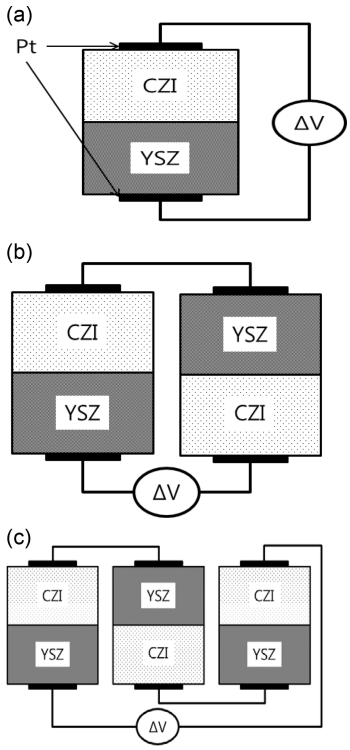

Fig. 1. Schematic structure of bi-electrolyte hydrogen sensors; (a) one-set, (b) two-set, and (c) three-set.

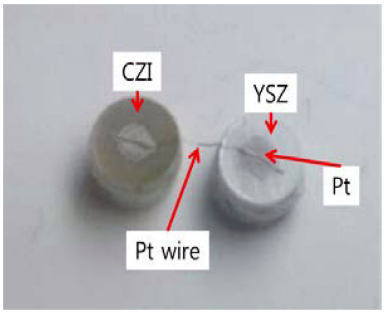

Fig. 2. A photograph of the fabricated sensor (two set).

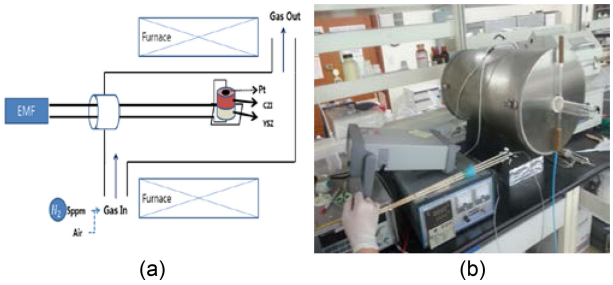

Fig. 3. Monitoring system of Hydrogen sensor; (a) Schematic structure and (b) photograph of the system.

selectivity for hydrogen, the sensitivity of the sensor in air was low because of the oxygen on the surface of $CaZr_{0.9}In_{0.1}O_{3-\delta}$ (CZI) [7]. Therefore, the sensors were connected in series using Pt wires to increase the sensitivity of the sensor by increasing the potential difference.

2. EXPERIMENTAL

2.1 Development of Hydrogen Sensor

The schematic structure of the hydrogen sensor is illustrated in Fig. 1(a). The structure of the sensor consists of two solid electrolytes and two platinum electrodes. The CZI electrolyte is made of a mixture of $CaCO_3$ (GCM, Korea), ZrO_2 (Aldrich), and In_2O_3 (Aldrich) powders. The CZI powder was prepared by the same method as reported in the previous study [8]. The YSZ electrolyte was prepared using yttria-stabilized zirconia (8 mol% Y_2O_3, Tosoh). A double layer of YSZ/CZI powders was pressed into a cylinder-shaped mold. The pressed heterojunction powder was sintered at 1600°C for 10 h. Platinum pastes were deposited on both sides of the bi-electrolyte and sintered at 1000°C for 1 h.

As shown in Fig. 1(b), each completed single sensor is composed of CZI and YSZ connected by the Pt wire, and the potential difference is measured between the outer ends of YSZ and CZI layers of each sensor. Similarly, three sensors were connected as shown in Fig. 1(c). A photograph of the fabricated sensor (two-set) is shown in Fig. 2.

The schematic structure of the hydrogen sensors and the monitoring system is shown in Fig. 3(a). The hydrogen sensing properties were evaluated in a quartz tube that was loaded in an electrical tube furnace at temperatures ranging from 450–600°C, as shown in Fig. 3(b). A mixture of 5 ppm hydrogen and air was prepared as a measuring gas. The total gas flow rate was fixed at 100 cm^3/min. The potential difference of the sensor was measured using a high impedance electrometer (Agilent 34972A).

3. RESULTS AND DISCUSSIONS

3.1 Sensing Mechanism

The hydrogen sensor with a bi-electrolyte structure was designed to measure the hydrogen concentration with respect to an oxygen reference, air in this case, where YSZ is adopted as an oxygen-ion conductor and CZI as a proton conductor. The designed electrochemical cell can be described as follows:

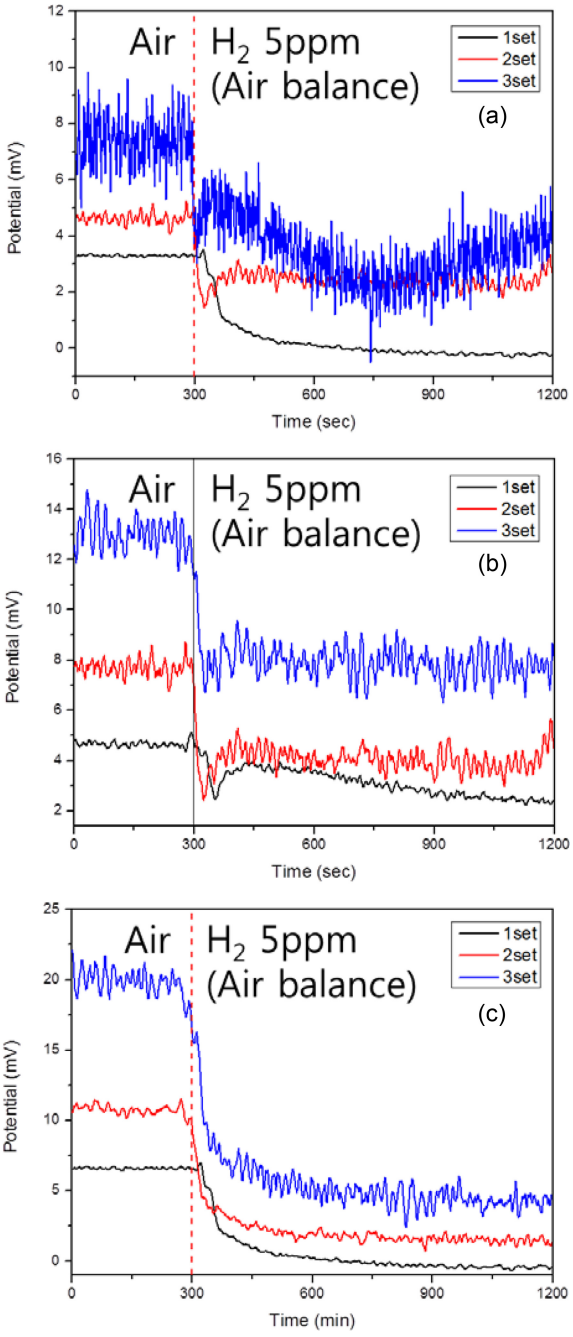

Fig. 4. Potential response of the sensor with 5 ppm hydrogen gas among connected number at reference at (a) 500°C, (b) 550°C, and (c) 600°C.

Pt, O_2 (0.21 atm) | YSZ || CZI | H_2, O_2 (0.21 atm), Pt (1)

At the sensing electrode on the right-hand side, the electrochemical reaction

$$H_2 = 2H^+ + 2e^- \quad (2)$$

occurs along with another simultaneous electrochemical reaction

Table 1. Potential difference by connected sensor numbers and temperatures

Temperature [°C]	1 set	2 SET	3 SET
500	2.5	3	4
550	3.5	4	6
600	6	8	14

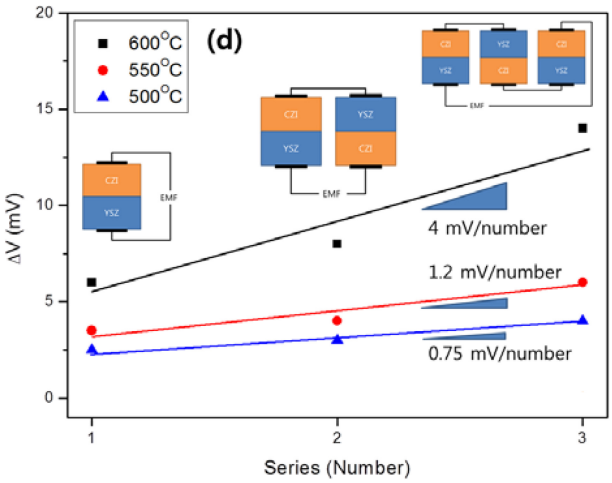

Fig. 5. Potential differences between the air state and 5 ppm of hydrogen as per the number of connected sensor and temperature.

$$(1/2)\ O_2 + 2e^- = O^{2-} \quad (3).$$

taking place at the reference electrode on the left-hand side. The overall cell reaction becomes a water formation reaction

$$H_2 + (1/2)\ O_2 = H_2O \quad (4)$$

The potential of the cell becomes

$$E = -\frac{\Delta G^O_{H_2O}}{2F} - \frac{RT}{2F}\ln\frac{a_{H_2O}}{P_{H_2}P_{O_2}^{1/2}} \quad (5)$$

where $\Delta G^O_{H_2O} = -247500 + 55.85T(J)$ and P_{H2}, P_{O2}, and P_{H2O} are the hydrogen partial pressure at the sensing electrode, the oxygen partial pressure at the reference electrode (= 0.21 atm), and the chemical activity of H_2O at the bi-electrolyte interface, respectively.

3.2 Sensing Performance

The sensors connected with multiple cells (two-set, three-set) were tested for 5 ppm (air balance) at 500, 550, and 600°C. Fig. 4(a), (b), and (c) show the response difference as per the number of connected sensors, i.e., Set 1, Set 2, and Set 3, respectively, upon exposure to 5 ppm of hydrogen concentration with corresponding

temperatures.

At each temperature, the potential difference increases with the number of series connections as shown in Fig. 4(a), (b), and (c). However, the noise of the signal increased as the number of connections of the sensor increased, as shown in Fig. 4(a), (b), and (c). The reason behind the noise could be the connection of the Pt wire, or an unstable contact point of the Pt wire connection for series connections.

The values of potential differences between the air state and at the state with 5 ppm of hydrogen are listed as per the number of connected sensors and temperatures in Table 1. Fig. 5 shows an increase in the slope with an increase in the temperature; 0.75, 1.2, and 4 mV for 500, 550, and 600°C respectively. The slope can be interpreted as a tendency of the sensitivity of the sensor increasing with respect to the increase in temperature. The potential difference increases linearly as the number of connections and the temperature increases.

4. CONCLUSIONS

A Park–Rapp probe was used in a hydrogen sensor that has a bi-electrolyte structure with a heterojunction along with a hydrogen ion conductor (CZI), and an oxygen ion conductor (YSZ). Even though the Park–Rapp probe shows an excellent selectivity for hydrogen, the sensitivity of the sensor was low when oxygen was on the surface of the sensor.

In the research, the sensitivity of the probe was improved by connecting the sensors in series for practical application. Therefore, the potential difference between air and 5 ppm of hydrogen was amplified even though oxygen and hydrogen existed in the same space. When more sensors are connected in series, the potential difference increases; however, noise also increases at each temperature level.

To further utilize the sensor as a leak detector, an effective method of reducing the noise and amplifying the signal should be considered.

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